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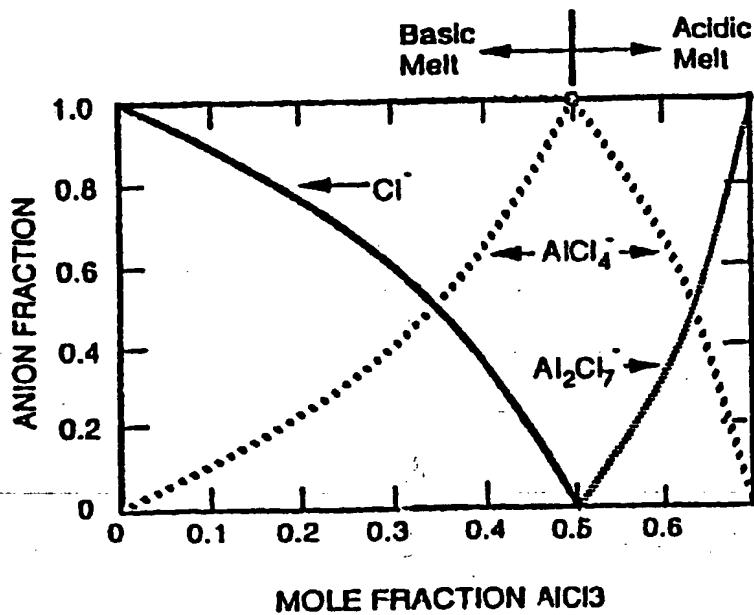
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(54) Title: PROCESS FOR THE EXTRACTION OF AN AROMATIC COMPOUND FROM AN ALIPHATIC PHASE USING A NON-NEUTRAL IONIC LIQUID

**Anion Fractions as a Function of the Mole Fraction of AlCl<sub>3</sub>**



(57) Abstract: Aromatic compounds can be removed from an aliphatic hydrocarbon fluid by contacting the fluid with a non-neutral ionic liquid that comprises a metal halide-derived anion.



PROCESS FOR THE EXTRACTION OF AN AROMATIC COMPOUNDS FROM AN ALIPHATIC PHASE  
USING A NON-NEUTRAL IONIC LIQUID

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Background of the Invention

Transition metals species (such as V, Ni, Ti or Fe porphyrin), nitrogen- and sulfur-containing (such as dibenzothiophene) compounds are normally present in crude oils. The concentration level of nitrogen and sulfur in gasoline and diesel fuel has been projected to be reduced to what cannot be achieved with existing technology without a large increase in cost. The current practice of employing a hydrodesulfurization catalyst has been found to be not effective for the desulfurization of dialkyl-substituted dibenzothiophene. The petroleum industry is under increasing pressure to reduce N and S level from fuels. In fluidized catalytic cracking units, heavy crude fractions are cracked using a zeolite catalyst. However, metals, such as V and Ni, in the oil are known to deactivate the catalyst by surface deposition and by causing structural damage. In addition, benzene is a known toxic aromatic component in the treated fuels.

Representative prior art approaches are described in the following U.S. Patent Nos.: 5,435,907; 5,449,452; 5,462,651; 5,472,595; 5,529,968; 5,556,824; 5,576,261; 5,651,878; 5,676,822; and 5,837,640.

U.S. Patent Nos. 4,422,634 and 4,440,634 to H.L. Mitchell describe the use of solid salt compositions, rather than ionic liquid compositions, to remove aromatics from aliphatic liquids.

A moisture stable ionic liquid, such as imidazolium hexafluorophosphate, is known to also be a solvent for the extraction of metal ions from aqueous solutions.

An ionic liquid comprising a metal halide and an 5 organic salt, such as imidazolium chloride, pyridinium chloride and alkyl ammonium chloride, is known to be an effective catalyst for benzene alkylation. A preferred catalyst of this type is trimethylamine hydrochloride which is described in U.S. Patent Nos. 5,731,101 and 5,824,832, 10 which are each incorporated herein in their entirety.

#### Summary of the Invention

The present invention relates to the use of a non-neutral ionic liquid that comprises a metal halide-derived anion for the extraction of aromatic compounds that may also contain heteroatoms such as sulfur, nitrogen, and metals from an aliphatic hydrocarbon fluid, such as a lubricant oil or a petroleum oil.

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#### Description of Preferred Embodiments

The present invention relates to the use of non-neutral ionic liquids that comprise a metal halide-derived anion (either a moisture stable or moisture sensitive ionic liquid, or mixture thereof) to extract aromatic compounds, for example those containing N, S, and metals, from such oil and fuel sources. The ionic liquid phase is immisible with the saturated lubricant oil or crude oil. By using the present invention, the oil or fuel can be effectively 30 cleaned using this ionic liquid treatment.

having the formula  $\text{Al}_2\text{Cl}_7^-$ . Furthermore, the molten compositions comprising this polynuclear ion are useful as described hereinbefore. Mixtures of more than one of these metal halides can be used.

5        Granular aluminum trichloride (+4 -14 mesh or having a particle size between 1.41 mm and 4.76 mm) can be an especially preferred metal halide to employ. It is easy to handle in air without fuming problems and has good flow properties. Its reaction with trimethylamine hydrochloride, 10 for example, is slower and more uniform than with aluminum trichloride powder, with a temperature exotherm to about 150°C. While the resulting ionic liquid is slightly hazy due to the presence of insoluble impurities from the aluminum trichloride, the insoluble, which settle out upon storage of 15 the liquid, do not have an adverse effect on the performance of the ionic liquid in regard to the process of the present invention.

One preferred class of organic base intended to be added to the metal halide to form the ionic liquid component 20 that is used in the process of the present invention is an alkyl-containing amine hydrohalide salt. The terminology "alkyl-containing amine hydrohalide salt", as used herein, is intended to cover monoamines, as well as diamines, triamines, other oligoamines and cyclic amines which 25 comprises one or more "alkyl" groups and a hydrohalide anion. The term "alkyl" is intended to cover not only conventional straight and branched alkyl groups of the formula  $-(\text{CH}_2)_n\text{CH}_3$ , where n is from 0 to about 18, preferably 0 to about 8, in particular 0 to 3, but other structures 30 containing heteroatoms (such as oxygen, sulfur, silicon,

aryl, if present, be comprised of carbon and hydrogen groups, exclusively. Such short chains are preferred because they form the least viscous or the most conductive melts. Mixtures of these alkyl-containing amine hydrohalide salts can be used.

The mole ratio of alkyl-containing amine hydrohalide salt which is to be combined with the metal halide is preferably, in general, range from above about 1:1 to about 1:2.5 so as to yield an acidic melt. In a highly preferred embodiment, the low temperature molten composition in the process of this invention consists essentially of the metal halide and the alkyl-containing amine hydrohalide salt.

Specifically, the most preferred, acidic, low temperature molten composition is a mixture consisting essentially of a mole ratio of trimethylamine hydrochloride to aluminum trichloride of from about 1:1.5 to about 1:2, preferably about 1:2.

Typically, the metal halide and the alkyl-containing amine hydrohalide salt are solids at low temperature, i.e., below about 100°C. at standard pressure. After mixing the two solids together, the mixture can be heated until the mixture becomes a liquid. Alternatively, the heat generated by the addition of the two solids will result in forming a liquid without the need for additional external heating. Upon cooling, the mixture remains a liquid at low temperature, i.e., below about 70°C, preferably below about 50°C, and more preferably below about 30°C.

The following Table illustrates typical melting points for a number of ionic liquid compositions and can be used in

hydrochloride		
Ammonium chloride	135 (AlCl <sub>3</sub> )	1/2
Tributylamine hydrochloride	-22 (AlCl <sub>3</sub> )	1/2
Amylamine hydrochloride	-50 (AlCl <sub>3</sub> )	1/2
Trioctylamine hydrochloride	-37 (AlCl <sub>3</sub> )	1/2
N-methylpyridinium chloride	125 (ZnCl <sub>2</sub> )	1/1
N-methylpyridinium chloride	95 (ZnCl <sub>2</sub> )	2/3

The advantages of using the type of low temperature ionic liquid described for use herein include having an easy-to-pump liquid employed in the reaction vessel and an extraction performance that does not depend upon the dissolution rate of a solid in the extracting liquid phase. 5 The extraction capability is much greater using an ionic liquid rather than a composition that is a solid phase material (as demonstrated in Example 4 and 5).

10 The minimum amount of ionic liquid that is preferably used to remove the aromatic compound component from the aliphatic fluid will be substantially equivalent to the stoichiometric amount of the target aromatic compound or compounds that are present in the fluid. The use of an excess of the ionic liquids is within the contemplation of 15 the present invention since any excess ionic liquids can be recycled and reused.

Example 2

Dodecane (10 gm) and 0.05 gm of naphthalene were weighed into a glass bottle. The resulting clear solution 5 was then analyzed by GC and was shown to contain 4713 ppm of naphthalene. Then, 5.4 gm of an ionic liquid comprising trimethylamine hydrochloride (TMAC)/Al<sub>2</sub>Cl, ionic liquid into the glass bottle containing the dodecane and naphthalene-containing solution. The solution was stirred for one half 10 hour at room temperature, and a sample of the clear solution above the ionic liquid layer was withdrawn and was analyzed by GC. The analysis showed that the naphthalene level in the clear solution had decreased 70% to 1496 ppm.

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Example 3

This Example illustrates a multiple step treatment in accordance with the present invention.

Dodecane (10 gm) and 0.05 gm of dibenzothiophene were 20 weighed into a glass bottle. The clear solution was then analyzed by GC that showed that there was 4772 ppm of dibenzothiophene in the background sample. Then, 3 gm of trimethylamine hydrochloride (TMAC)/Al<sub>2</sub>Cl, ionic liquid was added into the glass bottle holding the sample containing 25 the dodecane and dibenzothiophene. The resulting sample was stirred for one half hour at room temperature, and a sample of the clear solution above the ionic liquid layer was then withdrawn and was analyzed by GC. Analysis showed that the dibenzothiophene level in the clear solution had decreased 30 88% to 573 ppm. Then, 6.09 g of the dodecane clear liquid

Example 5 (Comparative Example)

This Comparative Example illustrates that the selection of tetrachloroaluminate as an anion, which produced a neutral composition in regard to either Lewis acidity or basicity does not remove aromatics from an aliphatic liquid.

5 Decane (10 gm) and 0.05 gm of dibenzothiophene were weighed into a glass bottle. The resulting clear solution was then analyzed by GC and was shown to contain 6049 ppm of dibenzothiophene. Then, 3 gm of an ionic "liquid" comprising trimethylamine hydrochloride (TMAC)/AlCl<sub>4</sub>, ionic "liquid" was placed into the glass bottle containing the dodecane and dibenzothiophene-containing solution. The trimethylamine hydrochloride (TMAC)/AlCl<sub>4</sub>, ionic "liquid" was 10 made from one mole of trimethylamine hydrochloride and one mole of AlCl<sub>3</sub>. It is a solid at room temperature.

15 The solution containing the solid phase ionic "liquid" was stirred for one half hour at room temperature, and a sample of the clear solution above the ionic "liquid" layer was withdrawn and was analyzed by GC. The analysis showed that the dibenzothiophene content in the clear solution had remained at the same level. The solid phase ionic "liquid" did not show any extraction capability. The clear decane solution containing the solid phase ionic "liquid" was then 20 heated to 90°C with stirring for one half hour. The dibenzothiophene level in the clear solution was analyzed by GC again. It showed that the dibenzothiophene level had remained the same after treatment at 90°C. The solid phase ionic "liquid" did not show any extraction capability even 25 when the system had been heated to 90°C.

Example 7

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The ionic liquid ( $\text{AlCl}_3/\text{TMAC} = 2:1$ ) prepared in Example 6, Part A was weighed into a glass bottle and then the selected model compound was added dropwise to the ionic liquid at room temperature. Control the speed of addition of model compounds so the temperature of the mixture can be kept below  $30^\circ\text{C}$ . The resulting mixture in the bottle was shaken for a few minutes to obtain a biphasic separation. The organic phase was then separated from ionic phase. The absorption capacity for each model compound was given in table 1:

The saturated hydrocarbons did not interact with the ionic liquid. Upon mixing, a clear two-phase solution was formed.

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Example 8

Follow the same procedure as described in Example II except that the ionic liquid made according to Example I B was used. The absorption capacity for each model compound 10 was given in table 2:

Table 2 shows the adsorption capacity of AlCl<sub>3</sub>/TMAC=1.5:1 for the selected model compound:

No	Chemical	M.W.	Added g	Removed g	Net IL, g	IL, g	Capacity, g/g IL, %
A1	2-Methylpentane	86.18	2.66	2.65	0.01	5.15	0.2
A5	1-Hexene	84.16	6.23	5.62	0.61	3.25	18.8
A7	Benzene	78.11	6.74	3.43	3.31	2.8	118.2
A8	Toluene	92.14	4.41	2.48	1.93	2.38	81.1
A9	Ethylbenzene	106.17	4.79	3.67	1.12	1.79	62.6
A10	Xylenes	106.17	4.03	2.31	1.72	2.82	61.0
A11	1,3,5-Trimethylbenzene(mesitylene)	120.2	3.26	2.7	0.56	1.28	43.8
A13	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> SH	90.19	1.73	1.41	0.32	0.94	34.0
A14	Thiophene	84.14	5.65	2.8	2.85	1.63	174.8
A15	2-Methylthiophene	98.17	2.56	1.7	0.86	2.86	30.1

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No interaction occurred between 2-methylpentane and the ionic liquid. Mixing of aromatics with the ionic liquid resulted in a slight color change to light yellow. Addition of 1-hexene into the ionic liquid resulted in formation of 20 brown solution initially and a light brown organic phase.

Addition of thiophene or 2-methylthiophene into the ionic liquid resulted in formation of a brown organic phase

Examples 9 - 15

5       Table 1 lists the sulfur content of gasoline and  
diesel samples received for the testing in Examples  
9-15.

Sample	Total Sulfur ppm*
Low-S Level Naphtha	220 (209.0)
High-S Level Naphtha	820 (793.0)
Low-S Level Gas-Oil	12,000 (12,122)
High-S Level Gas-Oil	250 (219)

\*numbers in brackets were given by supplier

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Example 9: Treatment of High-S Level Naphtha

In this Example, 5.95 g of an ionic liquid formed by  
15 mixing aluminum trichloride and trimethylaluminum chloride,  
"TMAC" ( $\text{AlCl}_3/\text{TMAC} = 1.5:1$ ) was mixed with 37.36 g of high S-  
level naphtha in a Pyrex flask under vigorous agitation at  
room temperature. The ionic liquid became light brown in  
one hour and was partially solidified. After separation  
20 from the ionic liquid, the liquid naphtha was analyzed by X-  
ray fluorescence. The total sulfur concentration was  
reduced by 54.9% (from 820 ppm to 370 ppm).

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Example 10: Treatment of High-S Level Naphtha

The same procedures were followed in this Example were  
described in Example 9 except that 3.71 g of the ionic  
liquid ( $\text{AlCl}_3/\text{TMAC} = 1.5$ ) was mixed with 43.3 g of high-S  
30 level naphtha. X-ray fluorescence analysis of the treated  
sample indicated a 42.7% total sulfur reduction (from 820  
ppm to 470 ppm).

Example 15: Treatment of Low S Gas-Oil

5.

The same procedures as described in Example 9 were used except that 5.74 g of the ionic liquid ( $\text{AlCl}_3/\text{TMAC} = 1.5$ ) was mixed with 44.07 g of low-S gas-oil. X-ray fluorescence analysis of the treated sample indicated a 28% total sulfur reduction (from 250 ppm to 180 ppm).

10. 15

Summary: Treatment Results for Ionic Liquid ( $\text{AlCl}_3/\text{TMAC} = 1.5$ )

Example No.	Ionic Liquid g	Untreated	Untreated g	S before Treatment ppm	S after Treatment ppm	S Removal %	Naphtha or Gas-oil /IL g/g
9	5.95	High S Naphtha	37.36	820	370	54.9	6
10	3.71	High S Naphtha	43.3	820	470	42.7	12
11	2.8	Low S Naphtha	46.51	220	130	40.9	17
12	3.79	Low S Naphtha	45.54	220	110	50	12
13	9.24	High S Gas-oil 652M	47.26	12122	8100	33.18	5
14	4.24	High S Gas-oil 652M	42.53	12122	9600	20.81	10
15	5.74	Low S Gas-oil 868	44.07	250	180	28	8
16	4.72	Low S Gas-oil 868	46.35	250	180	28	10

The foregoing Examples have been presented to merely illustrate certain embodiments of the claimed invention and, for that reason, should not be construed in a limiting fashion. The scope of protection sought is set forth in the Claims that follow.

8. The process of Claim 7 wherein the alkyl-containing amine hydrohalide salt is of the formula R<sub>n</sub>N.HX where at least one R group is alkyl and the metal halide contains a 5 metal which is selected from Group VIII, Group IB and Group IIB of the Periodic Table of The Elements.

9. The process of Claim 8 wherein the metal halide is ferric trichloride.

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10. The process of Claim 1 wherein the aliphatic fluid containing the aromatic compound is treated by the ionic liquid in multiple steps until the aromatic compounds are 15 substantially removed.

11. The process of Claim 1 wherein the contacting of the aliphatic fluid with the ionic liquid takes place at a temperature that ranges from about room temperature to about 20 150°C.

# INTERNATIONAL SEARCH REPORT

Int	tional Application No
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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 C07C7/10 C10G21/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7 C07C C10G		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 220 106 A (BOATE DOUGLAS R ET AL) 15 June 1993 (1993-06-15) cited in the application column 4, line 29 - line 30 column 4, line 35 - line 36 ----- US 4 359 596 A (HOWARD KENT A ET AL) 16 November 1982 (1982-11-16) cited in the application column 4, line 38 - line 40 column 4, line 45 - line 46; claim 6 ----- US 4 496 744 A (ATWOOD JERRY L) 29 January 1985 (1985-01-29) -----	1-11 1-11
<input type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.
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Date of the actual completion of the international search  12 March 2001		Date of mailing of the international search report  20/03/2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel: (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016		Authorized officer  Janus, S